

Comments on The April 17, 2002 ICCEC Approach to Silicofluorides Study

I. Introduction

The following documents were delivered to NIEHS (J. Bass) by Federal Express at 9:20 AM, August 14, 2002:

- (a) A letter dated January 18, 2002 attributed to Sally C. Gutierrez, Director Water Supply and Water Resources Division of the EPA indicating the EPA's intent to study dissociation of silicofluorides;
- (b) Three documents relating to "a" (i) an EPA solicitation to prospective bidders to provide assistance in the described subject area; (ii) an extensive survey of the "Fate" of silicofluorides in drinking water; (iii) a short discourse on research strategy;
- (c) Response by the undersigned to a publication issued and widely circulated circa 2000-2001 as an official work product of the EPA, ostensibly providing "proof" that the work contemplated above was unnecessary;
- (d) Comments by the undersigned on a self-congratulatory CDC MMWR report on water fluoridation;
- (e) Response by the undersigned to the ATSDR's solicitation for comments on a new fluoride profile;
- (f) Response by the undersigned to the EPA's solicitation for comments on new regulations for organophosphates as environmental toxins that operate by inhibition of cholinesterases;
- (g) A reprint of an article covering work by Professor Roger D. Masters and the undersigned published in NeuroToxicology;
- (h) A copy of a 1953 publication of the American Dental Association indicating the state of the art of fluoridation, with bland assurances of silicofluoride safety without tests;
- (i) A verbatim transcript of a two day meeting of fluoride experts convened in 1983 at the behest of Surgeon General Koop to review the state of their knowledge of health effects of chronic exposure to fluoridated water.

Each of these bears on the proposed NTP study of silicofluorides and will be discussed in Section III., below. Before that, however, it would be useful to comment on the "The Review of Toxicological Literature" dated October 2001 performed by personnel of Integrated Laboratory Systems ("ILS") and presumably used by the ICCEC in support of their proposed staged study of silicofluorides, defined as "Chemical characterization studies to assess chemical fate under aqueous conditions-Toxicological studies may be considered when results of chemical characterization studies are available for review"

II. ILS Review of Toxicological Literature [on silicofluorides for water fluoridation]

This is an impressive recitation of information that seems to be non-responsive to the central question: “What, if any, health effects can be expected from chronic human ingestion of potable water treated with sodium fluorosilicate or fluorosilicic acid (the silicofluorides or “SiFs”) as compared with those that are induced by chronic human ingestion of sodium fluoride (NaF) treated water?”

Fundamentally, the ILS Review seems to dismiss this issue altogether by citing two references (Crosby, 1969; and Urbansky and Schock, 2000) both of which claim that “essentially 100%” of either injected SiF dissociates into nothing other than “silicates” and free fluoride ion, so SiF-treated water must be “just like” NaF-treated water.

The unreliability of this assertion is treated at length in our document “c” and on pages 4 through 13 of document “e” so that issue will not be discussed here. However, the ILS literature study fails to mention the work of Masters and Coplan that prompted Urbansky and Schock to write their article in the first place. It seems rather odd that an article directly bearing on the issue at hand and which was published in a prestigious peer-reviewed widely-circulated journal (*NeuroToxicology*) was not worthy of note.

On the other hand, the ILS Review provides a plethora of irrelevant information such as the nature of the toxic gases that are emitted from crystalline solid sodium fluosilicate when it is heated to decomposition. This has no bearing on what toxins, if any, remain in potable water treated with commercial SiFs to produce the fluoride ion level supposedly optimal for prevention of caries.

Moreover, detailed discussion of commercial sources of the SiFs and their Material Safety Data Sheets adds nothing to the knowledge base pertaining to the usage of these compounds for water fluoridation and any known or suspected health effects from incompletely dissociated SiF residues.

The ILS review would have been more useful if it had discussed the test procedures prescribed by NSF for measuring SiF product quality and any health testing related to their use as water treating chemicals done under their “NSF 60” Standard, the supposed “bible” on that subject. In searching for this latter piece of information the ILS reviewers would have discovered that the NSF does no health testing itself and prescribes no specific health tests for SiF-treated water.

One is left with the impression that the ILS reviewers have dismissed out of hand the possibility of toxic effects from long-term chronic ingestion of incompletely dissociated SiF species at low dosage levels. This impression is not dispelled by their repetition of the naive idea purveyed by several NSF staff and some formal communications they have submitted to Congress that as long as “silicates” are below some threshold and “fluoride” is found at close to an expected 1.2 ppm, nothing else needs to be known about other dissociation products left behind in SiF treated water.

Another important mistake in the ILS review is its assumption that the realities of water fluoridation accord with some standard ideal process. The fact is that the nominal optimal fluoride level of 1 ppm is often exceeded in practice by a factor of two or more. The effect of this on the assumed concentrations of non-dissociated SiF species is very significant. The effect is even worse in cold climate areas where some water plant operators admit to having injected over 2 ppm of fluoride (from fluosilicic acid) without trying to adjust pH to off-set additional acidity. The notion that “natural buffering” is adequate for complete dissociation without side reactions (such as with alum) is unsound. The ILS study would have been better based on a few phone calls to learn the pragmatics of water plant operations rather than rely on idealized expectations.

The “bottom line” is that the ICCEC has made a poor decision if it used the ILS Review to justify its planned deferral of toxicology testing on laboratory animals pending the outcome of more work by Urbansky/Schock and their contractors. The next sections of this writing will show why allowing the EPA to devote a couple more years and a meaningful amount of money to find ways to justify their past mistakes would compound those mistakes. This approach can only be seen as a temporizing gesture without scientific justification.

III. The Documents FedExed to Dr. Masten

The assortment of listed material that was submitted is intended for consideration by those in a position to make decisions on the deferral of animal testing. Such work should be undertaken promptly, not put off pending completion of more exercises in theoretical inorganic chemistry. Conducting animal exposure experiments immediately is eminently justifiable considering the fact that the EPA has been floundering around for at least thirty years trying to make a case for allowing the use of a class of untested agents for water fluoridation. Their unwillingness to admit that straightforward toxicity testing is manifestly lacking and highly important should not be allowed to over-ride good science. The same must be said about those in the CDC who are responsible for implementing the national campaign to essentially compel the ingestion of SiF-treated water and food products produced with it. These observations will be documented here.

A. EPA’s acknowledged ignorance about a position they have adamantly held

Document “a” is tantamount to an admission by the EPA that Urbansky and Schock were incorrect in their attack on the findings of Masters and Coplan (Masters RD and Coplan MJ; “Water Treatment with Silicofluorides and Lead Toxicity”; *Int. J. of Environ. Studies*; 56; 435-449, 1999 and Masters RD, Coplan MJ, Hone BT, and Dykes J; “Association of Silicofluoride Treated Water with Elevated Blood Lead”; *NeuroToxicology* 21 (6), 2000). Nevertheless, the EPA seems intent on clouding the issue with a wet smog, as will be described next.

B. EPA’s continued effort at misdirection

Document “b(i)” (the EPA Request For Assistance) seems straightforward enough unless one is alert and reasonably informed about the science under consideration. On page 3 under “2.3.2. Analysis and measurement conditions” the RFA lists four categories of

“homoleptic and heteroleptic fluorosilicates,” one being “hexacoordinate,” that are to be studied. In that category, the RFA enumerates six specific species. The problem is that the RFA is singularly silent on the most important species belonging in that group and happens to be the one found in the PhD thesis work of Westendorf (Westendorf J; “Die Kinetik der Acetylcholinesterase Hemmung und Die Beeinflussung der Permeabilität von Erythrozytenmembranen durch Fluorid und Fluorocomplex-Jonen”; Doctoral Dissertation, Universität Hamburg Fachbereich Chemie; Hamburg; 1975).

This “incompletely dissociated” SiF residue also happens to be the one the undersigned has described and discussed in some of the other documents enumerated in the Introduction, above. The species $[\text{SiF}_2(\text{OH})_4]^{2-}$ is one of the more likely incompletely dissociated SiF residues to persist in SiF-treated water for reasons that are explained in other forwarded documents, but is NOT included in the list of “fluorosilicates” enumerated in the RFA authored by Urbansky.

Document “b(ii)” “The Fate of Fluorosilicate Drinking Water Additives” is a very comprehensive and useful effort by Urbansky to tell (most of the) important facts while still ignoring $[\text{SiF}_2(\text{OH})_4]^{2-}$ as a possible “incompletely dissociated” SiF residue. However, to give credit where it is due, one must acknowledge that he may have succumbed to an impulse to move in the direction of scientific candor and integrity in the “Conclusions and Unresolved Issues” section starting on page 29 which begins:

“There is considerable debate over the composition and even the existence of some homo- and heteroleptic aquo-, fluoro-, and hydroxo complexes of silicon (V), which makes it impossible to predict what species might be found in real potable water supplies that are fluoridated or those that naturally contain fluoride and silicates as background ions. The only agreement seems to be that hexafluorosilicate does not undergo cumulative, consecutive displacements of hydroxide for fluoride. Even this agreed-upon “fact” would seem to be drawn into question by some of the observations of partial hydrolysis in moist air, suggesting that the analytical tools were (are?) incapable of detecting the very low concentrations that might exist. *Given the disparity in the speciation models, there is hardly conclusive evidence that consecutive, cumulative substitutions of hydroxide for fluoride are impossible.*” (Emphasis added).

The italicized sentence is a concession (albeit grudging) that Westendorf may have been correct in having postulated the existence of $[\text{SiF}_2(\text{OH})_4]^{2-}$ in 1975 and Coplan in 2002 at page 10 of the document herein identified as “e.”

Document “b(iii)” (“Fluosilicate Research Strategy”) suggests that the impulse to apply scientific integrity has faded away. The opening sentence under “Background” reverts to form in both its language and substance. First, the work of Masters and Coplan does NOT implicate all fluoridating agents in elevated blood lead. We have carefully studied and freely emphasized the fact that NaF treated water is NOT associated with elevated blood lead according to the data we have analyzed. The over-arching bald “fluoridating potable water” is incorrect and should have read “fluoridating potable water with silicofluorides.”

Second, the use of the term “alleged” is totally inappropriate in scientific discourse. It is a snide way of implying that the results of well-founded epidemiological statistical analysis produced by someone who differs with the “established verities” of water fluoridation has somehow come to the party with unclean hands. In 1999 Urbansky collaborated in a scurrilous and widely disseminated attack on this work as “junk science” initiated by Tom Reeves, the CDC National Fluoridation Engineer. Apparently, that mind-set persists among some personnel at the EPA.

C. Why Urbansky and Schock Cannot Be Trusted

Document “c” should be read without further comment.

D. Why the CDC Cannot Be Trusted

Document “d” should be read without further comment.

E. An Urgent Need for The ATSDR to Do Its Homework

Document “e” should also be read, but special attention should be paid to the analysis of the Crosby data on pages 4-9. It is vital to understand why Crosby’s results for fluosilicic acid are untrustworthy. His “99%” dissociation at his supposed “1 ppm” of free fluoride is a mathematical artifact due to rounding off decimal point figures. The error is not in the amount of free fluoride Crosby actually measured. The error is in the denominator of the fraction in which his measured free fluoride is divided by an ostensibly “known” concentration of fluoride in the sample he tested.

There is every reason to believe that Crosby’s nominal “1 ppm” sample was NOT 1.0 ppm, but 1.34 ppm, produced by serial ten-fold dilutions of a stock solution of 134 ppm. It is one thing to drop the decimal digit “4” from 13.4 when the stock solution is first diluted ten-fold. The maximum error that decimal rounding produces in the end result of the division is only 0.4 parts out of 13.4, or about 3 %. That is, 10.0 divided by 13 yields 77 % and dividing 10.0 by 13.4 yields 75 %.

However, while dividing 0.99 by 1 yields 99 %, dividing 0.99 by 1.34 yields 73.9 %. Dropping the 0.34 after the decimal point creates an error of 34 parts out of 134, or 25 % in the end number. Crosby’s supposed 99 % dissociation of fluosilicic acid at “1 ppm” is badly flawed. Nevertheless it has been cited widely by the EPA and others. It seems that no one has independently verified that value on commercial samples of fluosilicic acid of unequivocally known SiF concentration diluted under strict control. Indeed, despite his table notation, in his Conclusions Crosby claims only 95% dissociation.

F. A Very Important Reason for Animal Studies

Document “f” repeats some of the material on SiF dissociation that appears in earlier listed documents, but adds a new dimension to the health significance of incompletely dissociated residues as AChE inhibitors.

G. The Elevated Blood Lead Story

Document “g” should be read in its entirety. Due note should be taken of the opening paragraph specifically relating the fact that the EPA could not find any evidence that work on health effects in humans from ingestion of SiF treated water had even been conducted. That reason alone should support prompt animal tests, whatever the EPA infatuation with theoretical chemistry may dictate. In addition, the references include the Westendorf thesis which should have been among the items addressed in the ILS Review.

H. Early Acceptance of Untested SiFs for Water Treatment

Document “h” deserves attention for its mere venerability. However, it also establishes without doubt that the use of silicofluorides began only 2 or 3 years after the first use of sodium fluoride in 1945. Whereas exposure of laboratory animals to sodium fluoride under various conditions had been studied extensively prior to 1945, there is no evidence that similar tests had ever been performed using commercial silicofluorides.

Contemporaneously with the many studies of fluoride as a dental health chemical, there was world-wide scientific interest in the possibilities for using radioactive chemicals in various ways. Much research, in fact, was devoted to healing health uses. Bathing in mineral baths carrying both fluoride and uranium radio-decay products (radium and radon) was often recommended as a health-restoration modality.

At the same time, in the mid-1930s, nuclear science had begun to develop into a new source for weapons of mass destruction. A so-called “dirty bomb” was conceived in which radio-active chemicals were mixed with ordinary explosives such as TNT. This approach, however, was quickly expanded into a more devastating concept...release of nuclear energy to create an explosion of incomparable intensity. US scientists in touch with refugees from Europe learned that German workers had made considerable progress in developing the fundamental theory.

On October 11, 1939, a mere five weeks after Hitler invaded Poland, a personal emissary delivered a letter to President Roosevelt from Albert Einstein dated August 2, 1939. That letter included the following relevant passage:

“The United States has only very poor ores of uranium in moderate quantities. There is some good ore in Canada and the former Czechoslovakia, while the most important source is Belgian Congo.”

The first US nuclear weapons used the Canadian ore. Much politicking was devoted to getting uranium from central Africa, but in the long run the “very poor” US ores would have to be used. That ore was the phosphate rock from which fertilizer phosphate is produced. The technology for extracting phosphate and uranium from “rock phosphate” included the ineluctable generation of by-product silicon tetrafluoride gas. It couldn’t be released into the atmosphere without devastating impact on the surface environment.

It could be collected in water to produce fluosilicic acid, but that couldn't be pumped down deep wells without contaminating the water supply systems of the area. It couldn't be loaded into ships and dumped at sea without destroying the ocean ecology. But billions of gallons of municipal wastewater capacity was available throughout the United States. What better way to get rid of fluosilicic acid than to dilute it with the water supplies of thousands of US communities?

It is important to note that page 18 of the document identified as “h” describes how the Federal Security Agency virtually barred the FDA from conducting tests on fluoridated water and food-stuffs prepared with such water. This kind of action is not taken without involvement of policy makers in the Oval Office. By 1952, SiFs were already beginning to supplant NaF for fluoridation.

I. The EPA Has A Precedent for Its Poor Track Record on SiFs

Document “i” is the verbatim transcript of a two-day meeting of health experts convened in 1983 at the behest of the EPA to help settle questions about enforcing upper limits on fluoride in drinking water. It deserves all the time that it takes to wade through. It is impossible to summarize all the reasons for that observation without quoting the transcript extensively. However, the letter from Surgeon General Koop to Secretary Ruckelshaus summarizing the experts' conclusions should and can be quoted because of its relevance to the issues under consideration here:

“Adverse health effects were defined by the committee as death (poisoning), gastrointestinal hemorrhage, gastrointestinal irritation, arthralgias, and crippling fluorosis.”

The work of this panel of experts has often been cited as exonerating chronic ingestion of fluoridated water as a possible contributing cause of adverse health effects. But, this severely limited list of “adverse health effects” is never quoted. Moreover, the expert panel never even began to consider the effect of different fluoridating chemicals.

Regarding that, there is one passage relating specifically to why animal health tests of SiFs are long overdue. It begins at page 132 and reaches a climax at page 140. It is noteworthy that in 1983 water fluoride was about 90 % due to addition of silicofluoride. The principal speaker being quoted is Frank A. Smith. His biography was found at

<http://www.urmc.rochester.edu/Miner/HOM/SMITH.HTM>

and reads as follows:

“On 10 June 1944, shortly after receiving his Ph.D. in physiological chemistry (i.e., biochemistry) from Ohio State University, Frank Ackroyd Smith (1919-1994) joined the Manhattan Project at the University of Rochester. Smith became a member of the Fluoride Laboratory of the Industrial Hygiene Section, part of the Manhattan Project's Division of Pharmacology & Toxicology. The laboratory

had been initiated in 1941 by Ann Tarbell, Ph.D., who headed the unit when Smith arrived, but who left the following year to raise a family. From then on Frank Smith headed both the Fluoride Laboratory and the Clinical Chemistry Laboratory of the Industrial Hygiene Section.

Initially the Fluoride Laboratory's purpose was to determine the fluoride content of urine samples collected from industrial personnel at Manhattan Project sites across the United States. Isolating needed isotopes from uranium ore exposed workers to hydrofluorides, tetrafluorides and hexafluorides which required monitoring. Occasionally the Laboratory was required to do fluoranalysis of bone samples for autopsies. Much of the initial work for determining bone fluorides was established in the Fluoride Laboratory at this time. The Laboratory can also be credited for having developed a successful analytic methodology for measuring fluoride in human blood, which had previously been very difficult to determine.

With the closure of the Manhattan District, the Division of Pharmacology and Toxicology continued to function under the aegis of the newly formed Atomic Energy Commission. The Fluoride Laboratory in Rochester provided fluoranalysis for the AEC nationwide.

As interest in water fluoridation increased in the mid-1950s, Smith began joint research on fluorides with Harold Hodge. Hodge had long been involved in dental research, and also headed the Division of Pharmacology and Toxicology for the AEC from 1948 to 1958. The field of fluoride metabolism was largely virgin ground when Smith and Hodge began their investigations into fluoride absorption, distribution and excretion.”

Clearly, anything Smith knew about silicofluorides would also have been known by his close collaborator, Harold C. Hodge. And H. C. Hodge is one of the authors of an article that appeared in 1957 (Feldman I, Morken D and Hodge HC; "The State of Fluoride in Drinking Water"; *J. Dent Res.* Vol 36 (2); 192-202, 1957) that begins with this passage:

“The widespread use of sodium silicofluoride in fluoridating drinking water has made it important to determine the state of the fluoride in such water, specifically, how much is fluoride ion, how much, if any, is unchanged silico-fluoride, how much is fluoride bound to other ions. If all or nearly all of the fluoride is the ion F^- , the great body of information about the biologic effects of fluorides can be brought forward as a guarantee of safety. If considerable amounts of silicofluoride remain, a question can legitimately be raised since comparatively little work has been done on the biologic effects of silicofluorides. This paper presents some experimental results permitting the conclusion that no silicofluoride exists in drinking water.”

This report in which this statement appears is important for several reasons:

1. It establishes unequivocally that the use of SiFs began without health effects testing.

2. It means to “prove” that water treated with SiF and NaF must be bio-actively identical but only shows that in 1957 SiF users were adding tons of a substance to the drinking water of the US public with no evidence of its health safety at the concentration they would be drinking.

3. Despite this fact, the authors of the article mean to “guarantee” the health safety of SiFs not by animal tests, but by theoretical chemical predictions of SiF dissociation.

4. The report was prepared by researchers whose scientific mission had nothing to do with tooth decay and everything to do with radiation medicine at a time when nuclear weapons were uppermost in the minds of the public and all national political figures.

5. While employing purely theoretical chemistry to prove that SiFs are harmless, the report qualifies its “guarantee” of health safety with language reminiscent of the term used at the time with regard to exposure to radiation, to wit: “...results *permitting* the conclusion...” of health safety. And it does so, despite admitting the possibility of a 40% error in the main calculation which produces that conclusion.

In 1952 (Wollan M; “Controlling The Potential Hazards of Government-Sponsored Technology”: The George Washington Law Review; V 36 No. 5; pages 1105-1119; July 1969) Congress requested health effects studies of inorganic fluorides that have yet to be performed on SiFs, as admitted by the highest EPA authorities in 1999 and 2000.

Despite information known to the US PHS in 1950 (McClure FJ: “Availability of Fluorine in Sodium Fluoride vs, Sodium Fluosilicate”; Public Health Reports vol 65 No 37; September 15, 1950, pp 1175-1186) showing a meaningful difference in health-related effects between chronic ingestion of SiF treated water and chronic ingestion of NaF treated water, the use of SiFs expanded rapidly after 1947. The problem did not go entirely unattended, however. The US PHS was interested in human excretion of fluoride from NaF treated water vs SiF treated water. (Zipkin I et al; “Urinary Fluoride Levels Associated with Use of Fluoridated Water”; Pub Hlth Rpts 71 pp 767-772; 1956).

For obvious reasons it was reasonable and acceptable to collect male urine. Two communities were compared over several years from the date of initial fluoridation until urine fluoride level and water fluoride level reached equilibrium. Four male populations were sampled: boys and older males in a community that had started fluoridating with NaF and a like pair of young and older male groups where fluoridation had begun with SiF water treatment. Two meaningful effects were observed in pooled urine samples from the four different groups of males.

First, equilibrium between urine and water fluoride concentrations was reached very quickly for the older males in each community compared to the boys in that community. This is logically explained by the fact that the body weight of the older males was pretty stable over the time of the experiment and there was little bone replacement by re-modeling going on. On the other hand, the body weight of the boys was changing and to a large extent this meant accretion of bone tissue with attendant uptake of fluoride.

Second, apart from the fact that the time to reach equilibrium for the boys was much longer than for the older males, the time to reach equilibrium for the boys ingesting SiF treated water was five years while the time for the boys ingesting NaF treated water was only three years. The relevance here is that this experience dispels the assumption that chronic ingestion of SiF treated water has no health effects different from those due to chronic ingestion of NaF treated water.

Quite possibly, F. A. Smith was the only man at the 1983 conference recorded in document “i” who understood this. Nevertheless, he did not object to a remark by one of the others that “fluoride is fluoride.” He also did not explain the “deltaF” phenomenon as clearly as he could have. The gaseous form of fluoride exposure his student’s animals had experienced may well have been due to silicon tetrafluoride rather than HF which would account for the polymeric nature of the unidentified fluoride-bearing species discovered in the animals’ blood. This subject deserves extensive re-investigation.

IV. Summary and Conclusion

A substantial body of evidence has been submitted to the NTP clearly supporting the need for a comprehensive program of animal testing for health effects from chronic ingestion of SiF treated water. This is true now and would remain true no matter what the EPA may learn about dissociation chemistry from a contractor selected by EPA employees whose objectivity and scientific integrity are less than impeccable.

V. A Personal Note

The undersigned is a registered Professional Chemical Engineer (Mass # 16331). His principal field for over twenty years was water and waste-water treatment with membrane systems in which he holds 2 dozen patents. Among the projects he supervised from about 1981 until his retirement in 1987 was a laboratory and on-site field study of membrane applications to deal with phosphate fertilizer production products and waste by-products. The latter category included pond water contaminated with radionuclides and fluosilicic acid. Thus, his knowledge of the situations and details recited herein includes first-hand contact with the substances and the problems they represent. The idea that silicofluorides collected as by-product fluosilicic acid should ever be fed to humans is appalling.

Beyond that view, however, the undersigned has been intensely exposed to the unseemly politics of water fluoridation. He served on his town (Natick) Board of Health during a period when water fluoridation was a major issue in contention. Independently of this, he became a “student” of the subject, making many contacts with recognized authorities in the field of dental disease and fluoride therapeutic modalities including 1940s work at the Tufts Dental School with effective topical fluoride treatments.

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